

N 8 6 - 2 6 6 9 6

D17-44  
P-19

A SILANE-BASED POLYSILICON PROCESS

8690

Paul E. Grayson  
Eagle-Picher Industries, Inc.  
Miami, OK.

EA 518989

James Jaffe  
Allied Corporation  
Morristown, N.J.

A 108712

INTRODUCTION:

Commencing in early 1981, a joint development program to pilot demonstrate a silane based polysilicon process was constructed at Eagle-Picher Laboratories in Miami, Oklahoma. The pilot plant included technologies contributed by Allied Corporation of Morristown, New Jersey, Eagle-Picher Industries of Miami, Oklahoma, and G. A. Technologies, Inc. of San Diego, California. The described process as piloted included the synthesis of crude silane gas, ultra purification of the gas, and then direct pyrolysis to product silicon. Features of the process provided for direct continuous operation from process feed to final product, without the requirement to store intermediates or ever convert the silane to a liquid phase. Semiconductor quality product as analyzed internally, and confirmed by independent laboratories, was demonstrated by the first integrated operation of the plant.

The project organizational responsibilities were as shown in Figure 1. The pilot plant described by this paper was constructed by the engineering and technical staff of the participating companies in residence at the Miami, Oklahoma site. The results of the first integrated operation of the plant as evaluated by Monsanto, are as shown in Figure 2.

The process development, although considered by all participants to be technically and financially very successful was abandoned in late 1982 for business reasons unrelated to this project.

ALLIED PROCESS:

In early 1980 Allied was considering making fumed silica from by-product fluosilicic acid on a large scale. Fluosilicic acid is formed in a phosphoric acid plant when the silicon tetrafluoride from the main rock digester is scrubbed. Large quantities of fluosilicic acid are available and much more could be made available if a market existed. Phosphate rock contains about 3.5% fluorine and about 30 - 50% of that fluorine can be recovered as fluosilicic acid.

The silicon tetrafluoride is produced from fluosilicic acid by reaction with strong sulfuric acid, which acts as a dehydrating agent.



PRECEDING PAGE BLANK NOT FILMED

The hydrofluoric acid can be further reacted by the addition of silicon dioxide



Allied looked at possible routes to photovoltaic silicon and decided to pursue two paths. The first was the use of high temperature plasma to react to the silicon tetrafluoride with hydrogen.



This route was considered the most desirable since Allied is the largest merchant producer of hydrofluoric acid in the U.S. No by-product would be produced.

A contract was let with Columbia University, who had an operating thermal plasma, to develop feasibility. The plasma process could not get greater than 5% yields of silicon, as it was not possible to quench the reactor products before most of the fine silicon recombined with the HF.

Concurrently, the reaction of sodium hydride with silicon tetrafluoride was investigated at Allied's Morristown, New Jersey laboratories.



A process was discovered that gave high yields of silane at moderate conditions. The silane was of high purity, as could best be determined by standard analytical procedures.

This process is covered by U.S. Patent No. 4,374,111 dated February 15, 1983.

With silane, it was apparent that purification could be effected by many methods and a literature search revealed that considerable work had been done. Allied decided that the immediate future of silicon lay in semiconductor grade, although it would be desirable to have a process that could produce silicon cheap enough to compete in the photovoltaic market. Allied made plans to pursue the necessary research to purify silane, produced from  $\text{SiF}_4$ , and the subsequent decomposition of the purified silane into semiconductor grade silicon.

At about this time, Allied was approached by Eagle-Picher to investigate the possibility of a joint venture to produce semiconductor silicon. Eagle-Picher had a process to purify silane and had also contacted General Atomic, who were in position to develop a process for the decomposition of the purified silane.

In a surprisingly short period of time, the three-party venture was approved and an agreement reached on a joint pilot plant to produce 1 kg. per hour of semiconductor silicon. The pilot was built at Eagle-Pichers'

Miami, Oklahoma facility. Allied's facility included two units. Photographs of the units are in Figure 3 and 4.

The first unit produced silicon tetrafluoride from purchased fluosilicic acid. Figure 5 shows how this was accomplished.

Fine sand was added to the fluosilicic acid which was then sent to a silicon tetrafluoride reactor. The sulfuric acid was fed to the top of the reactor and product  $\text{SiF}_4$  was compressed to 300 psig for storage. The outgoing waste sulfuric acid was practically free of fluorides and was sent to waste disposal.

Yields were almost stoichiometric and the purity level of the  $\text{SiF}_4$  was very high. Capacity of the small unit that was built exceeded design by more than 200%.

In a commercial plant the fluosilicic acid would come from an adjacent plant or tank car and the sulfuric acid would be returned to the fluosilicic acid producer or other user.

In Figure 6, the proposed commercial silane operation is shown. Hydrogen returned from the silane decomposer plus make up hydrogen is reacted with sodium to form sodium hydride. This reaction is done in mineral oil.

The sodium hydride slurry in mineral oil is fed to the silane reactor where it reacts with silicon tetrafluoride to form silane gas. The solvent used is a commercially available high boiling material, like diphenyl ether. The reactor runs at about  $250^\circ\text{C}$  and slightly above atmospheric pressure. Yields on sodium hydride and silicon tetrafluoride were demonstrated to be greater than 90% in the pilot plant. It is believed that with optimization this could be raised somewhat.

The silane produced was of good quality, with small impurity levels. Design capacity was exceeded and the reliability of the process was demonstrated.

#### PURIFICATION PROCESS:

The process developed by Eagle-Picher for silane purification was motivated by the low cost photovoltaic project being conducted by JPL at that time. A number of years earlier Eagle-Picher had looked at the feasibility of separating the isotopes of boron by the technique of large scale preparative gas chromatography (LSGC), but had abandoned the concept in favor of liquid exchange. With the advent of the JPL project, the prospect that large quantities of photovoltaic grade silane might be available led to the investigation of the method as a means to ultra purify the gas to the extent of semiconductor quality. Further, to do so very safely and economically, thus establishing the possibility of a competing process to Siemens, which had put Eagle-Picher out of the silicon business some 25 years earlier.

Gas Chromatography (GC) is widely employed as an analytical tool to separate components of a volatile mixture. The several components are then characterized, both qualitatively and quantitatively, with one of a wide variety of detectors. The heart of such an instrument is the chromatographic column. Figure 7 shows the action of such a column. The column consists of a length of stainless steel pipe packed with particles of very uniform size and composition. An inert gas, called the carrier, passes through the column. The mixture to be separated is introduced as a small batch, or injection, into one end of the column. In Figure 7, the sample is composed of three components represented by squares, triangles, and circles. As the mixture is pushed through the column by the flowing carrier, the various components interact differently and so percolate through the column at differing rates. If the operator has been clever about selection of the particles with which the column has been packed and the values of the various operational parameters, the components of the mixture will be separated by the time they exit, or elute, from the end of the column. As the mixture percolates through the column, the molecules become mixed with carrier gas and the concentration of the component in the carrier gas assumes a near-Gaussian distribution.

Figure 8 is a block diagram of the large scale GC (LSGC) used for the purification of silane gas. Carrier gas is supplied to the column through standard regulators and flowmeters. Silane pulses are periodically admitted into the column by a computer operated valve. At the end of the column is a hot wire detector which registers the passage of any gas with a thermal conductivity different than that of the hydrogen carrier gas. Immediately following the detector is the gas flow system is a switching valve that routes the GC effluent to one of several lines. In our silane system, there were two such lines: a waste line going to a flare and a pure line going to the silane collection system. In normal LSGC useage, the components of interest are separated from the carrier gas in a condensor at this point. In our system, we were interested in retrieving only a hydrogen mix of the silane, so the condensor was eliminated. Carrier gas is recycled through a cleaning system consisting of carbon scrubbers, molecular sieve traps, and catalytic deoxygenators. The switching of all valves is done on a timed basis. A dedicated valve sequencer module is used for this purpose. The system employed in the effort described in this paper was a commercial unit heavily modified for use with mixtures of silane and hydrogen, and shown in Figure 9.

Nearly 60 different column packing materials were tested for silane use. A set of gas mixtures composed of silane, hydrogen, argon, oxygen, nitrogen, carbon dioxide, water, diborane, arsine, phosphine, silicon tetrafluoride, and the various chlorosilanes were used for this testing. (No one mixture contained all of the various samples). The concentration of the sample gases ranged from 30 ppm to 2% in either silane, hydrogen, or helium. Best success was obtained with a porous polymer, Poropak. A composite chromatogram of these materials is shown as Figure 10. Two one meter sections 80 mm in diameter were packed with this material. The separation was done at essentially room temperature and typical throughputs of 1200 grams per hour were obtained at the optimum operational parameters. Eagle-Picher has a patent pending on the system as described.

The purified silane/hydrogen mixture was compressed into specially cleaned carbon steel holding containers. A two-stage triple stainless steel diaphragm compressor was used for this compression, and is shown in Figure 11. A surge tank between the LSGC and the compressor was found necessary.

The measurement of the purity of the silane proved to be as difficult a technical problem as the purification itself. The silane was converted to silicon and the resulting silicon was used to grow Czochralski crystals of comparable purity to those obtained from Siemens material. The various impurities present could be attributed to either the pure silane, the conversion process, or the crystal growth. This leads to a great deal of uncertainty to the quality of the silane as purified by LSGC. The assumption appears justified that the silane is equal to or surpassing conventional Siemens polysilicon.

The silane was also characterized by analytical gas chromatography. Work done in our laboratories utilized the hot wire detector and the flame ionization detector. The hot wire detector is sensitive down to about 10 ppm, depending on the identity of the impurity. No impurities were found in the purified silane with this detector. The flame ionization detector proved useless for the analysis of the silane, even when the silane itself was routed around the detector to prevent silicon oxide formation on the internals of the detector. In addition to the work done in our laboratory, samples of the purified gas were sent to an outside laboratory for GC/MS analysis. Again, no impurities were detected, even when concentrations were used.

The silane was further characterized by growing epitaxial films of silicon from the gas and subjecting the films to spreading resistance profiling. The substrates used were low boron antimony doped silicon wafers. The antimony doping was used to demark the interface between the substrate and the film. Antimony was used because it was felt that less diffusion into the growing film would occur than with other dopants. Growth of films was done in our laboratory and also contracted to SDI, a manufacturer of electronic devices. All of the films were profiled for net carrier concentration at Solecon Laboratories by the spreading resistance technique. A bevel was ground on the films, then the film was profiled by stepping the probe at regular intervals down the bevel. A resulting profile is shown as Figure 12. Nearly all of the films tested showed carrier concentrations in the range of  $10^{12}$ , with about a 50% variation. This was true for two different feedstock materials of assumed differing starting impurity composition. These profiles indicate that all films are either of very high purity or nearly perfectly compensated.

The work described in this paper indicates that silane gas may be purified by the technique of LSGC. The purity of the silane is enhanced beyond the limits of commonly used analytical tools. Epitaxial films indicate the gas may be of very high purity. Direct analytical methods need development to confirm this indication.

The method for pyrolysis piloted by General Atomic Technologies will not be discussed in this paper at their request.

The economics of producing semiconductor quality silicon by the combined process is as shown in Figure 13.

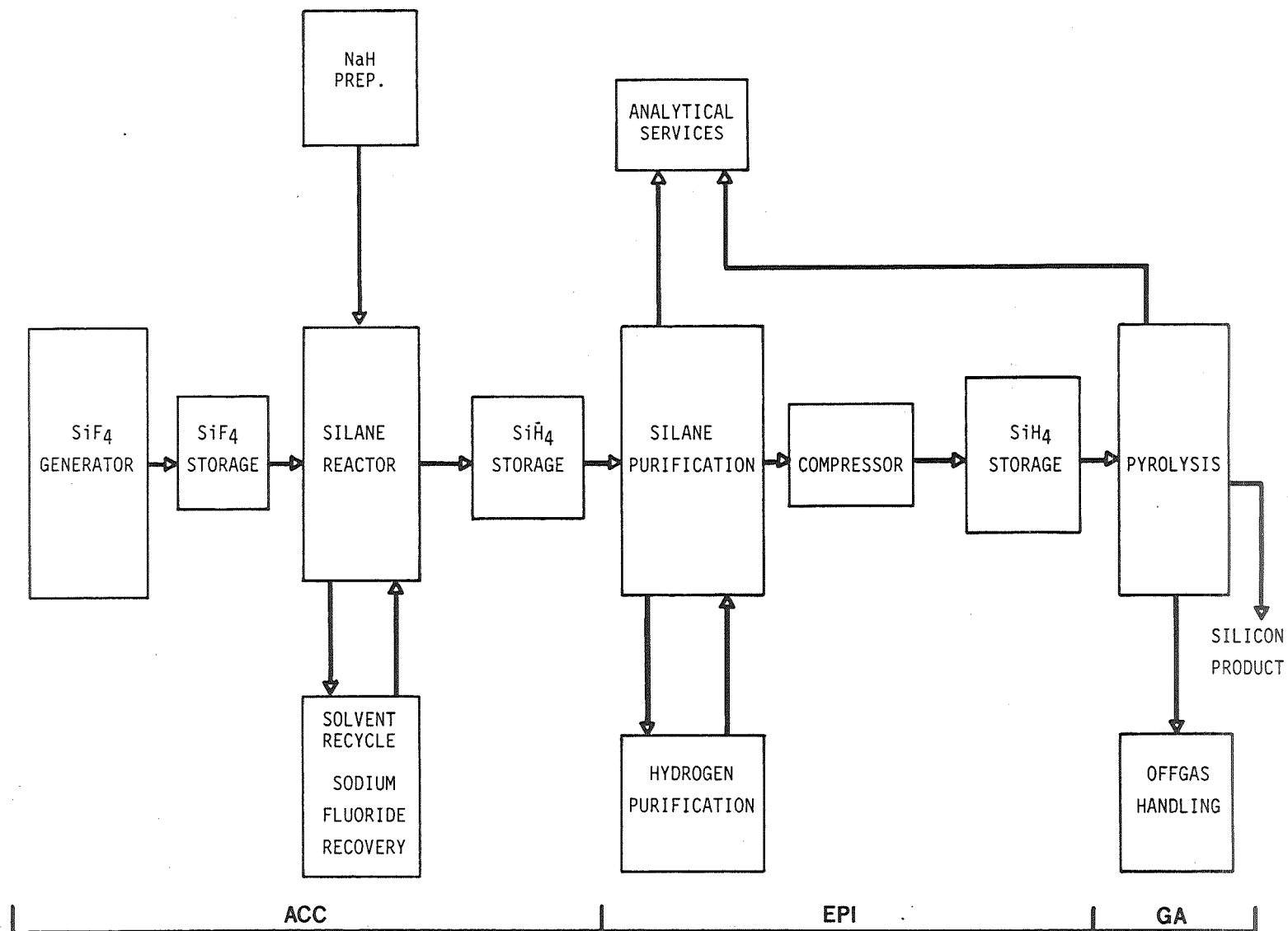


FIGURE 1  
PROJECT ORGANIZATION

# EAGLE-PICHER POLYSILICON - CRYSTAL EVALUATION

	#PULLS FOR "Z-D"	RESISTIVITY (ohm cm)	CONDUCTIVITY TYPE	P-L ANALYSIS (ppba)				CARBON (ppma)	LIFETIME (μ secs)
				B	P	Al	As		
E-P 1 *	1	2000	P	1.2	1.1	0.1	0.04	4.8	300 +
E-P 2 *	2	2500	P	1.5	1.4	0.2	0.09	2.6	300 +
TYPICAL SIEMENS	1 or 2	200 to 5000	90% N	0.3 to 1.0	0.5 to 1.5	AS ABOVE	AS ABOVE	<0.3	300 +

\* CRYSTALS: ~ 2 INCH DIAMETER X 6 INCHES LONG.

FIGURE 2  
FIRST PILOT PRODUCTION



ORIGINAL PAGE IS  
OF POOR QUALITY

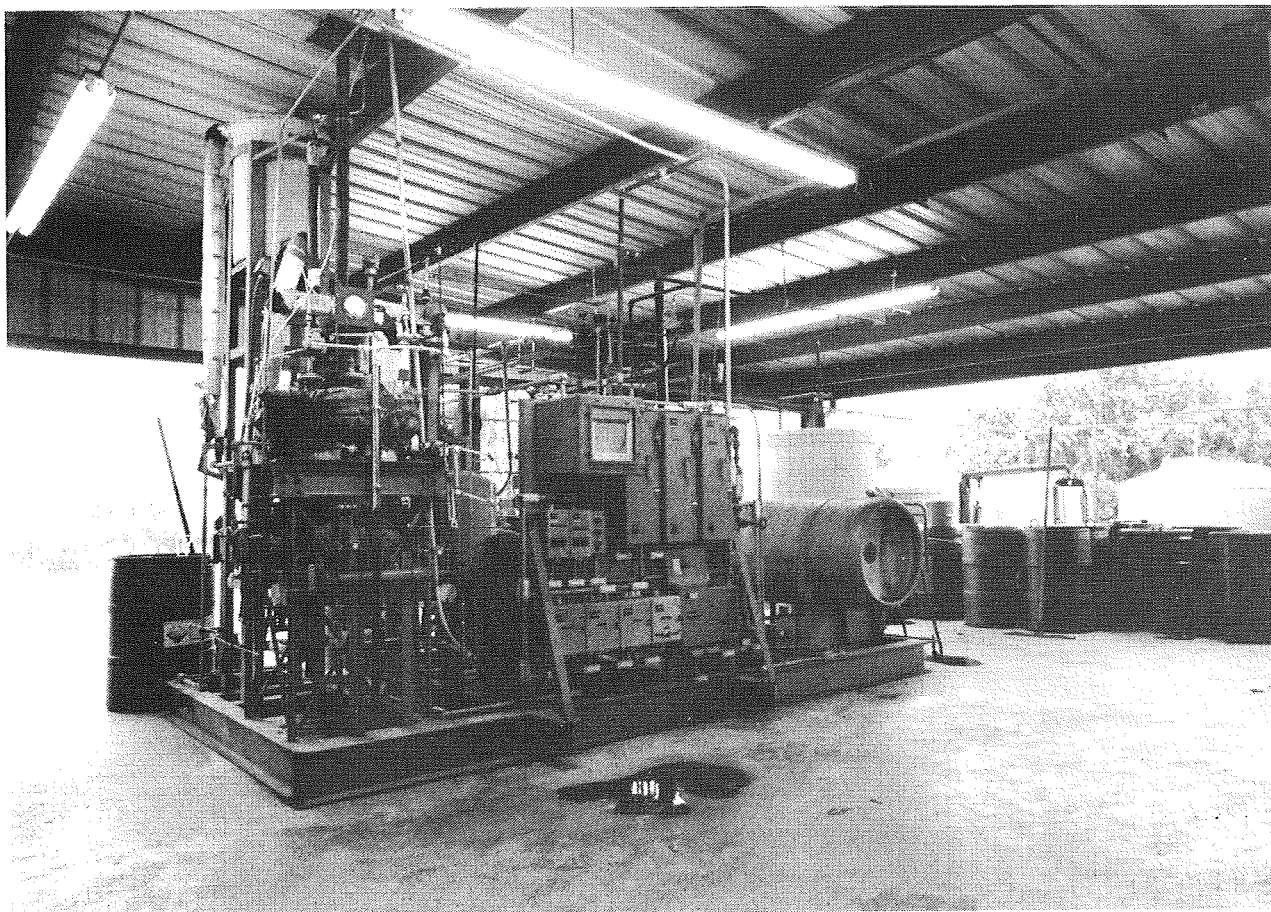


Figure 3  
Pilot Plant  $\text{SiF}_4$  Generator Skid

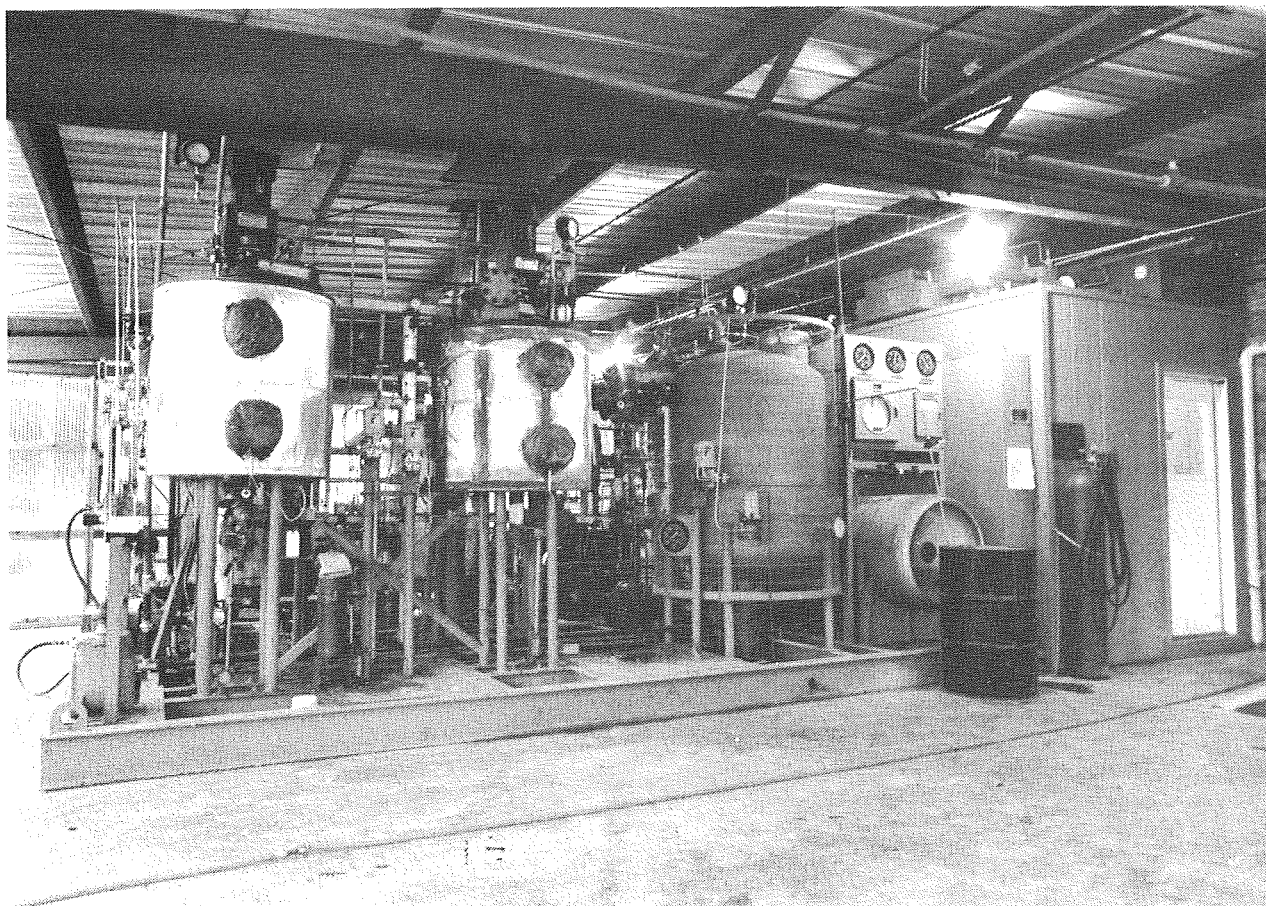


Figure 4  
Pilot Plant SiH<sub>4</sub> Generator Skid

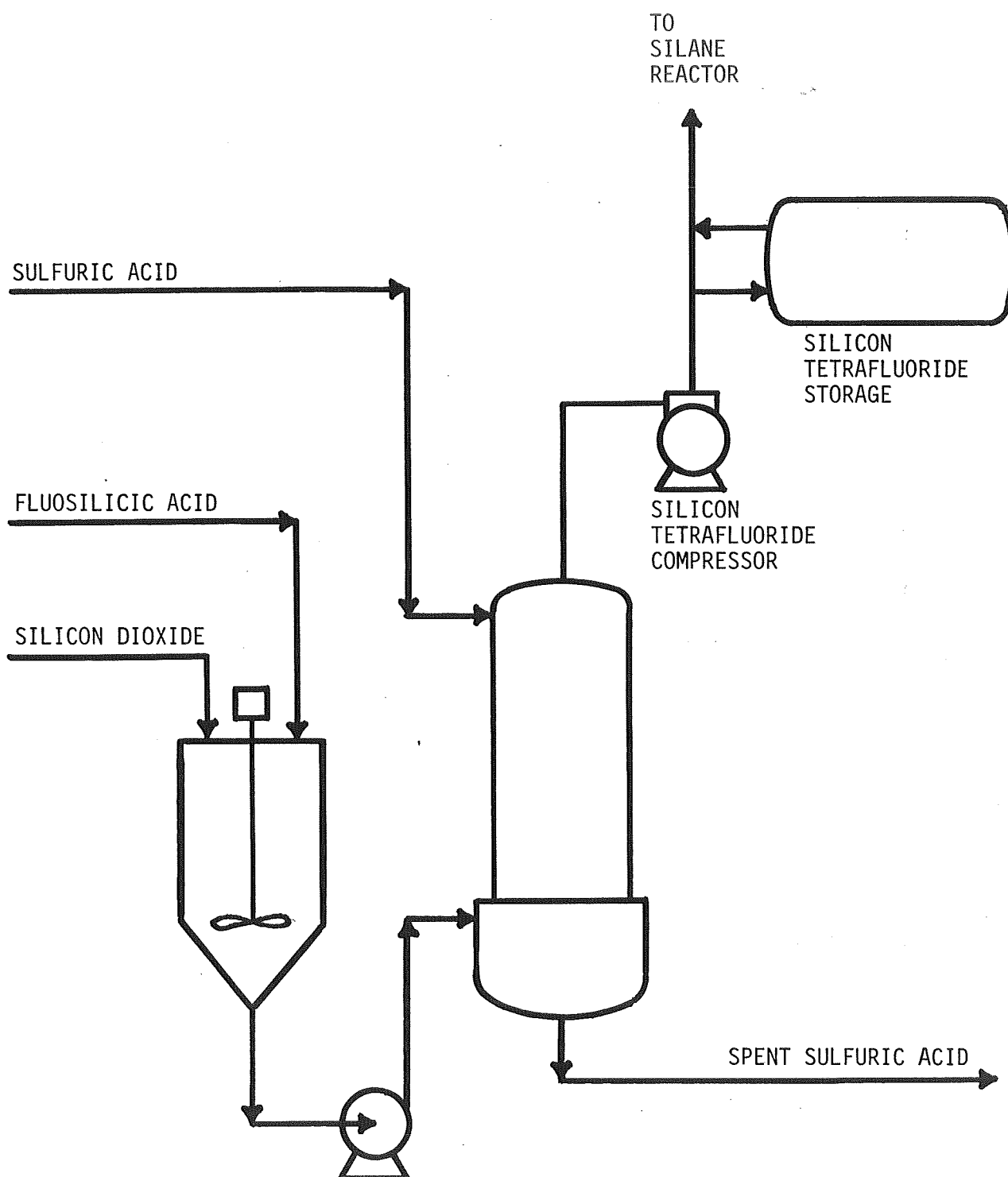


FIGURE 5  
 $\text{SiF}_4$  PROCESS

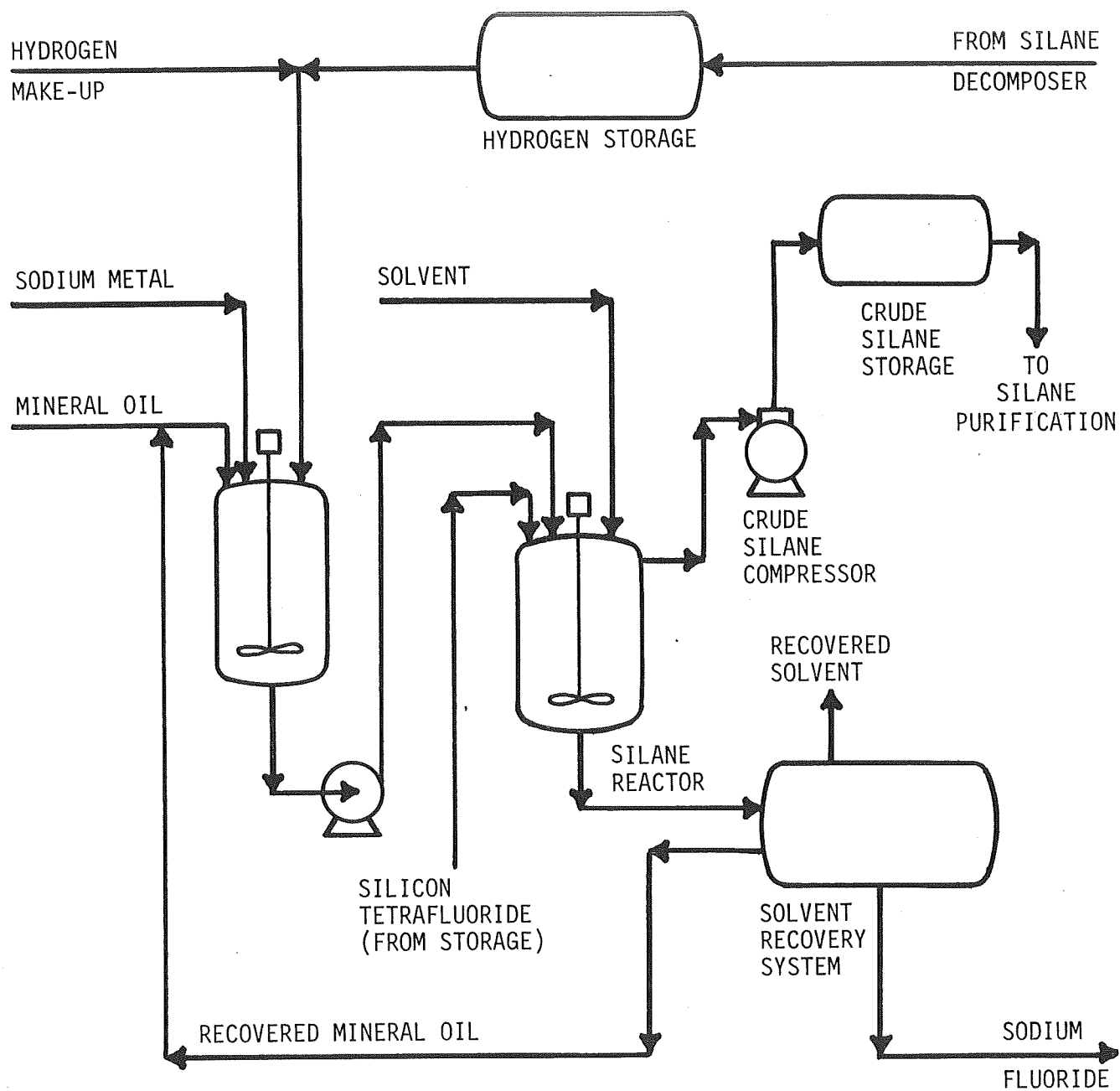


FIGURE 6  
 $\text{SiH}_4$  PROCESS

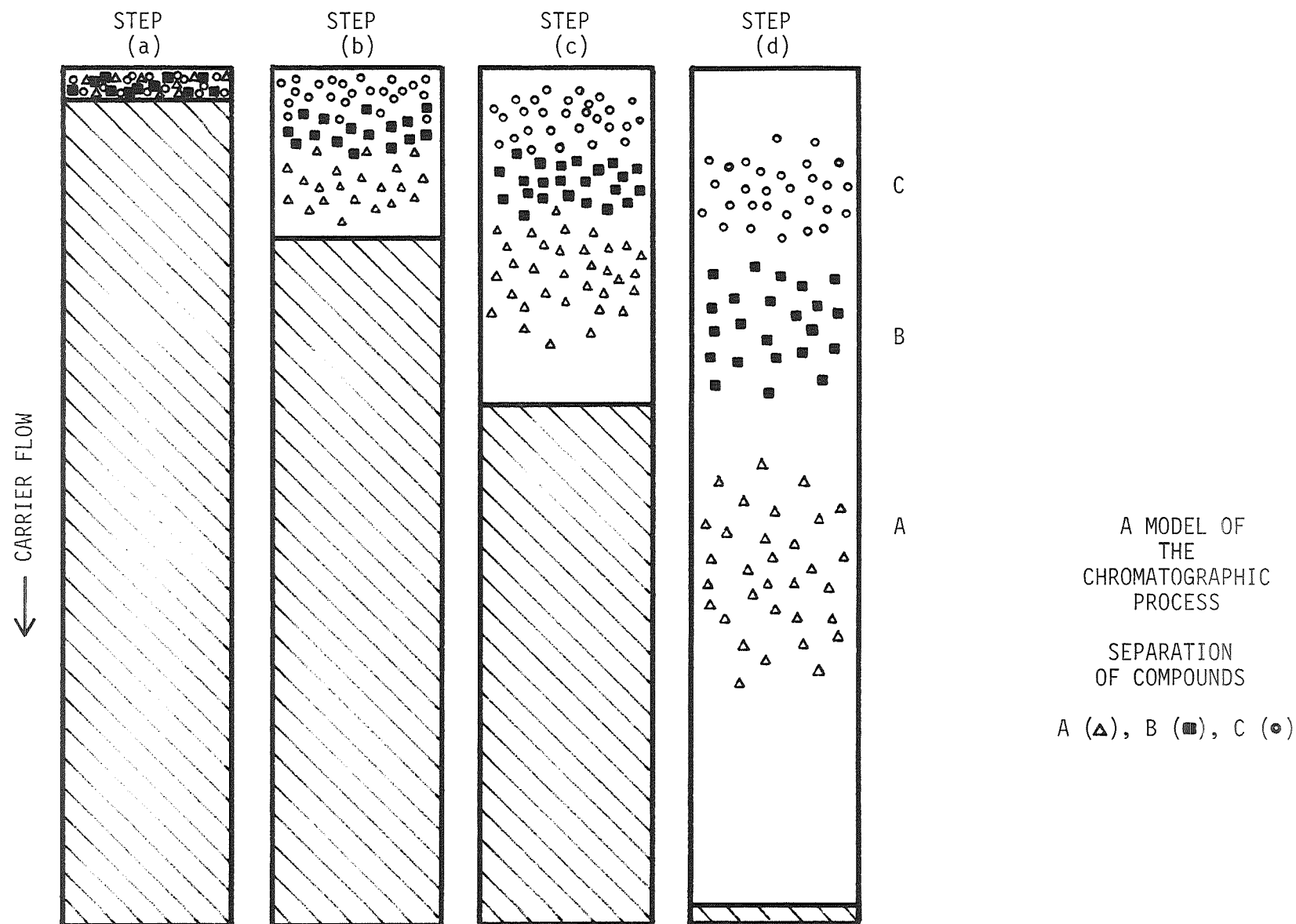


FIGURE 7

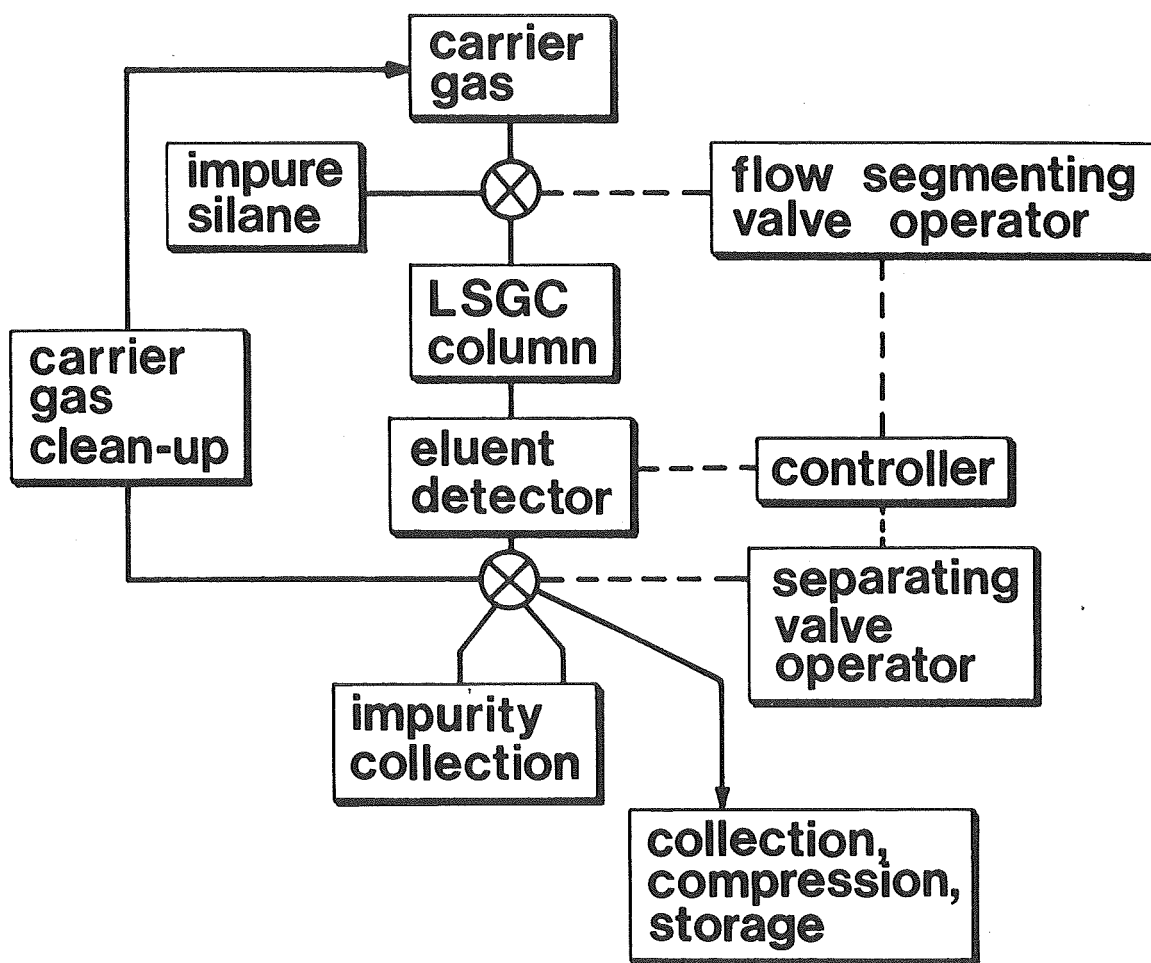


FIGURE 8  
LSGC PURIFICATION PROCESS FLOW

ORIGINAL PAGE IS  
OF POOR QUALITY

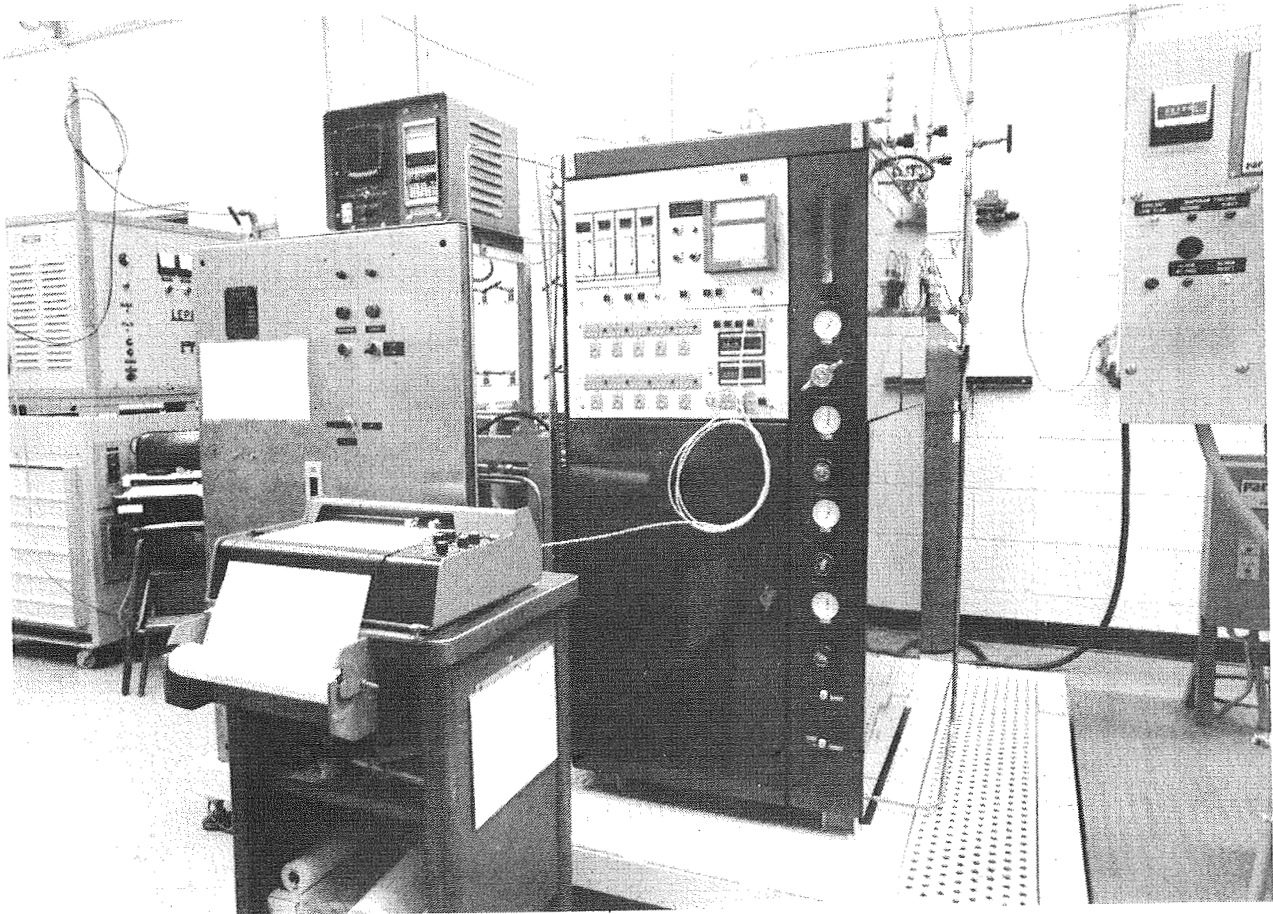


Figure 9  
LSGC Pilot Plant

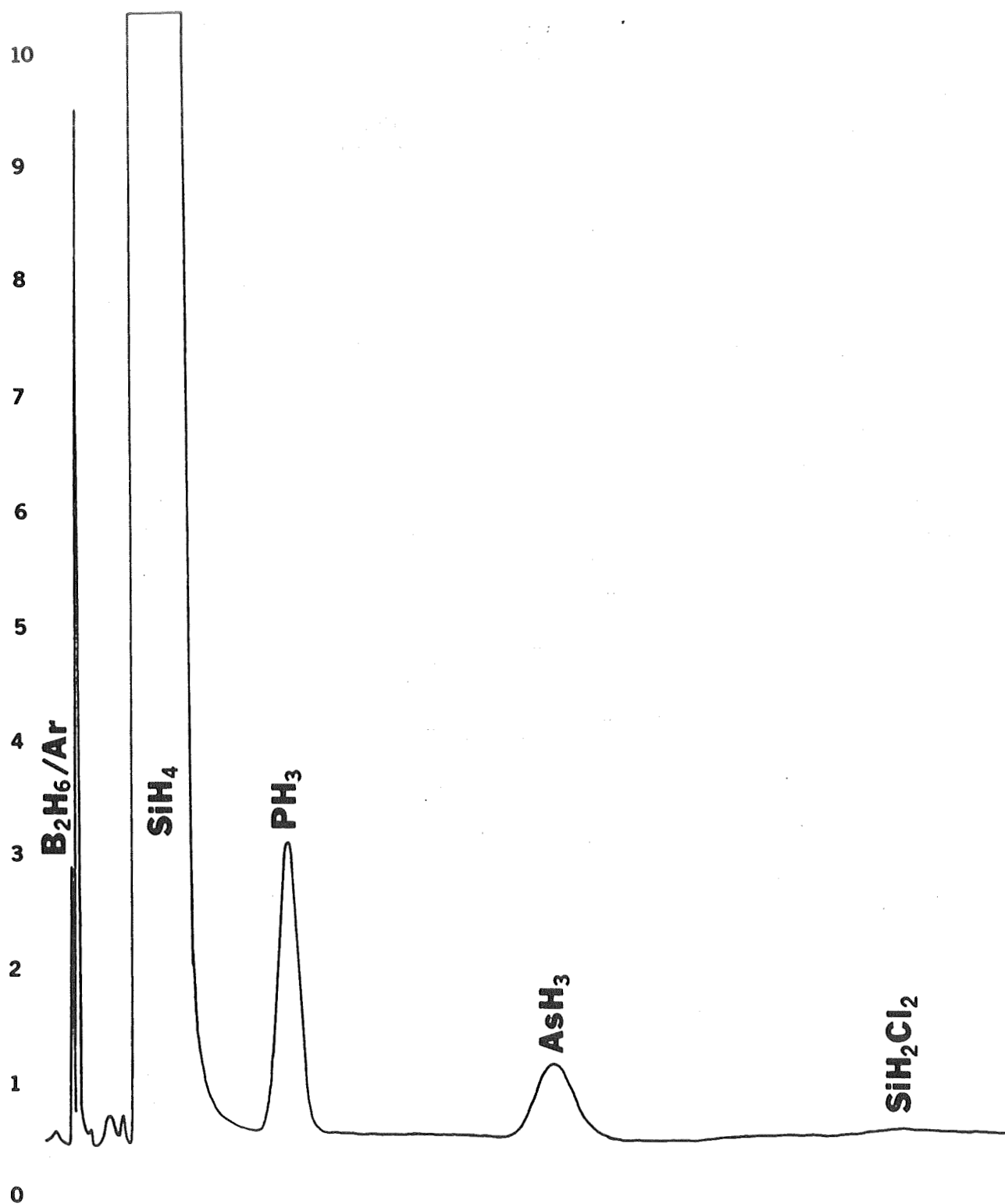


FIGURE 10  
TYPICAL G. C. IMPURITY PROFILE



ORIGINAL PAGE-15  
OF POOR QUALITY

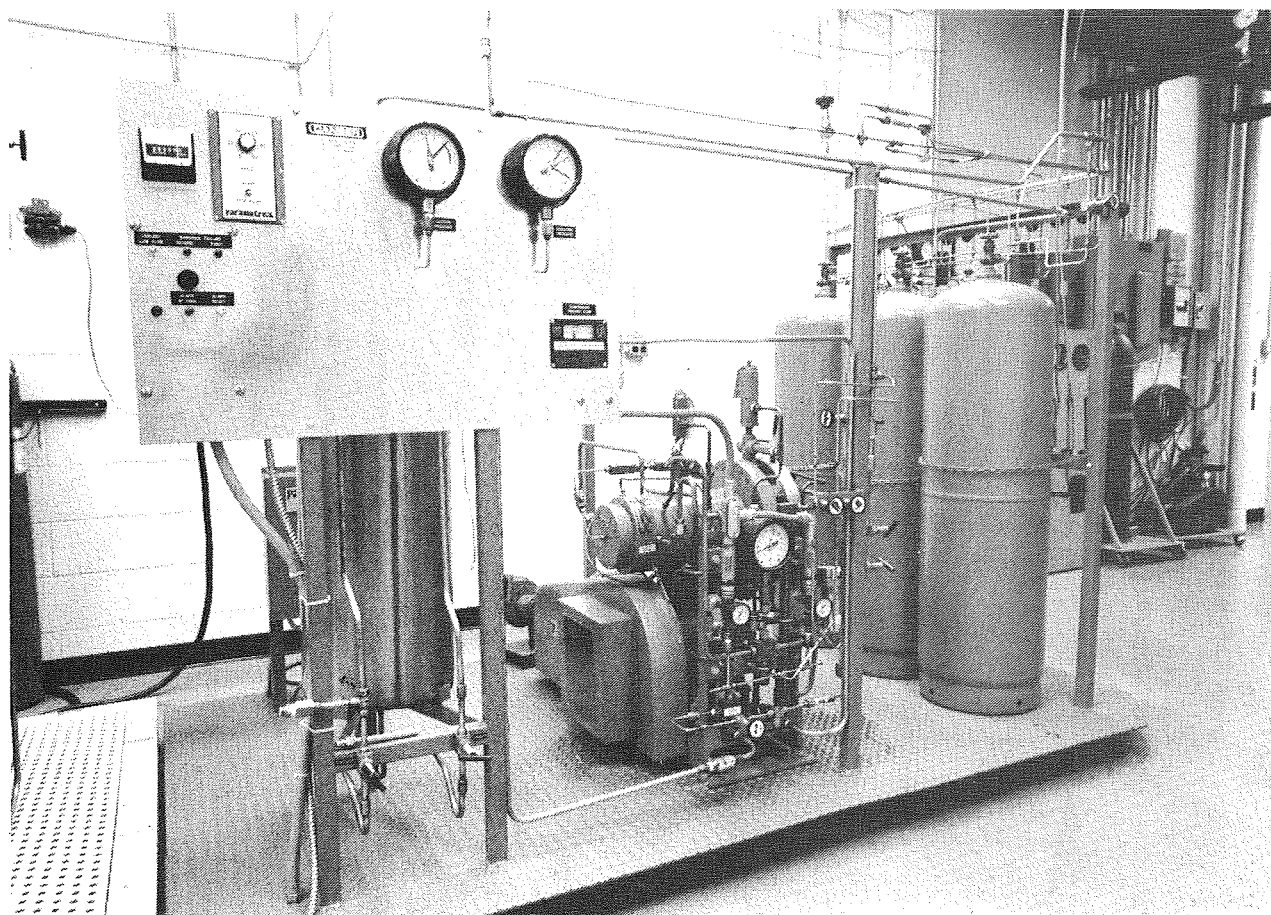


Figure 11  
Picture of Compressor

SPREADING RESISTANCE ANALYSIS

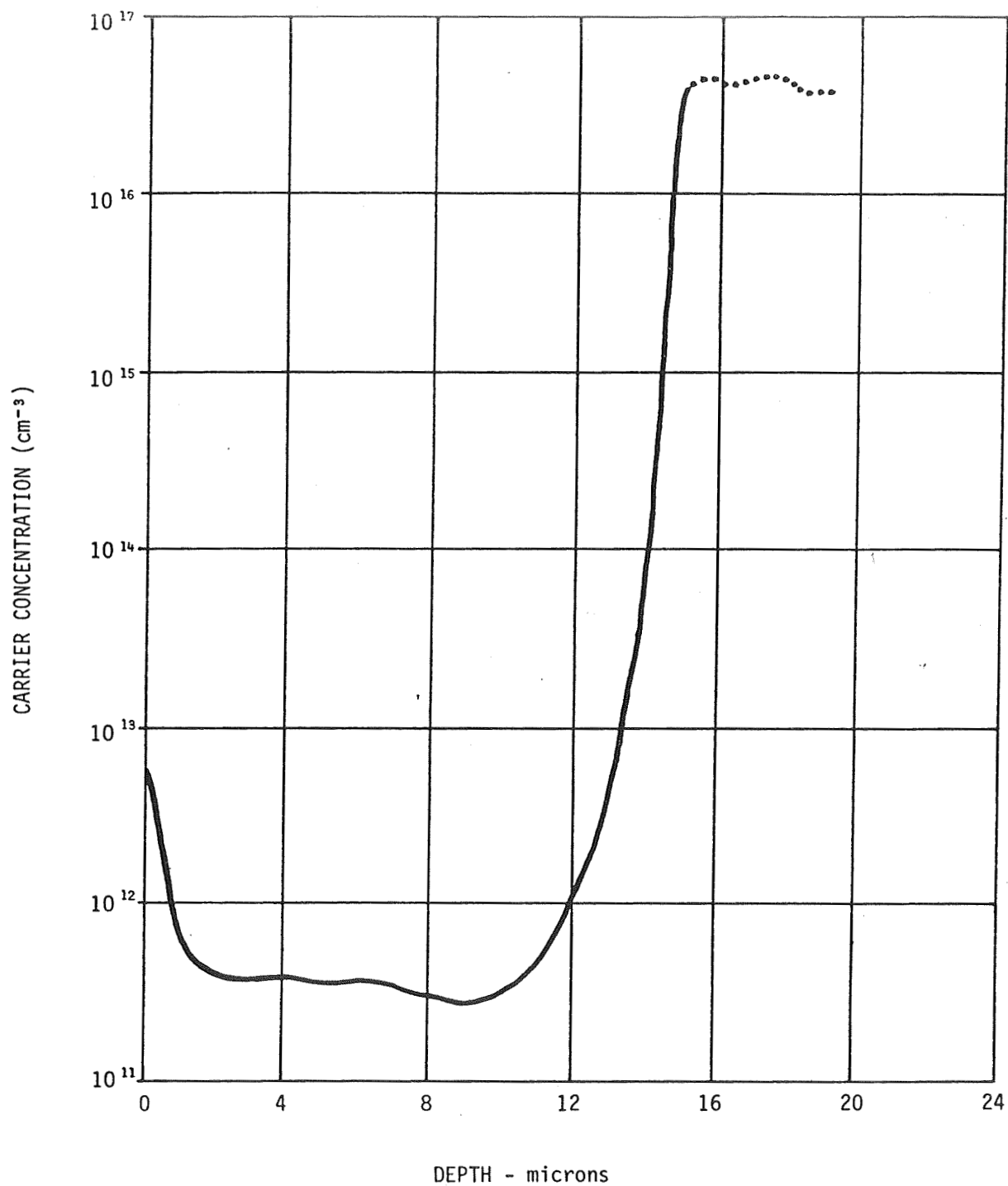


FIGURE 12  
ANALYSIS OF EPI-SILICON FILM  
GROWN FROM LSGC PURIFIED SILANE

## CAPITAL AND MANUFACTURING COST ESTIMATES

### FOR

### POLYSILICON FACILITY

#### BASIS

- o Capacity 1000 Metric TPY
- o Grass roots facility
- o Based on  $\text{SiH}_4$  from  $\text{SiF}_4$  via Allied's process
- o Involves purification of  $\text{SiH}_4$  and decomposition to polysilicon
- o 1983 Dollars

#### CAPITAL

Fixed capital is estimated at \$40MM which includes:

\$5MM for the  $\text{SiF}_4$  facility;

\$10MM to produce crude  $\text{SiH}_4$ , and

\$10MM for off-sites

Of the total of \$40MM, 15% is engineering/project management and 10% is contingency.

#### MANUFACTURING COST

Raw Materials	\$8.25/Kg Si
Productive Labor & Supervision	1.25
Depreciation (10% of Capital)	4.00
Maintenance (5% of Capital)	2.00
Taxes (1.5% of Capital)	0.60
Utilities	1.50
Plant Administration	0.50
Test & Inspection	0.45
Miscellaneous	<u>1.00</u>
TOTAL	\$19.55/Kg Si

FIGURE 13

DISCUSSION

HSU: What throughput was demonstrated for the large-scale gas chromatographic unit for the silane portion?

GRAYSON: It was a 1200 gm/h throughput for the GC column we had.